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Lignin hydroconversion on MoS_2-based supported catalyst: Comprehensive analysis of products and reaction scheme

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ABSTRACT

The hydroconversion of a wheat straw soda lignin was studied in a batch reactor, in tetralin solvent, with a $NiMoS/Al_2O_3$ catalyst under H_2 pressure at 350 °C. Gaseous, solid and liquid products were separated, quantified and detailed analyses were performed in order to describe and to understand the various reactions occurring versus residence time. In those operating conditions, the weakest β-O-4 and α-O-4 ether linkages of the lignin were first cleaved. The lignin was thus progressively converted into smaller hydrogenated and deoxygenated fragments called lignin residues which were extensively characterized by GPC and NMR. In the liquid phase, smaller monomers and dimers were identified by GC × GC/MS and quantified by GC × GC/FID. The evolution of these molecules was investigated as a function of residence time in order to investigate the catalytic transformation scheme of lignin.

1. Introduction

Lignin is one of the organic substances which constitute wood and cell wall of plants with cellulose and hemicellulose [1]. Being the second most abundant biomass component, lignin is also a unique aromatic-based natural resource which can be the precursor of aromatic and phenolic compounds for the chemical industry [2,3]. This natural macromolecule is a by-product in the pulp/paper industry and nowadays it is only burned as a low-value fuel. In addition to this industrial sector, which represents a production of 50–80 million tons per year, lignin will be soon available in even larger amounts via the emerging technology of 2nd generation cellulosic ethanol production obtained through the enzymatic route, yet at industrial level with a few commercial units being built and in operation in the world [4]. Depending on its origin and on the process used to isolate the lignin, its structure can vary a lot and the development of a universal and efficient transformation way of lignin into a valuable bio-liquid is becoming a great challenge. In addition to biochemical and oxidation conversion routes, several types of thermochemical degradation methods [5,6] have been proposed so far for the lignin depolymerization and lead to 20 to 70 wt% of liquid yield based on the dry biomass. Looking at the literature, it appeared that an interesting way to obtain high yield of liquid products was the use of classical hydrotreating catalyst in presence of a hydrogen donor solvent [7–10] as proposed in liquefaction processes yet used for coal conversion to liquid fuels [11]. The use of this kind of solvent strongly reduces the recombination reactions and the formation of char and tar and thus increased bio-oil yield [12]. Meier et al. have also performed hydropyrolysis of the lignin without any solvent to evaluate the residence time, temperature and catalyst effect without any solvent influence [13]. Following those investigations, Thring et al. realized the catalytic conversion of a solvolytic lignin in tetralin solvent and underlined the need for H_2 pressure to achieve higher liquid yield and lower the solid residue coming from dehydrogenation reactions [14]. Some other type of H-donor solvents as formic acid [15] or alcohol [16] were also proposed and allowed to obtain high yield of liquid. Concerning the catalytic systems employed for the lignin depolymerization, besides conventional supported metal sulfides [7–10,17], zeolites [18], metal chloride [19,20] and supported metals [21,22] were also tested, sometimes in a two-step process being helpful [23]. It was often assumed that high quantity of the phenolic monomers or gasoline-like alkanes can be obtained, however, deep and appropriate characterizations, as well as the mass balance were not always reported. Effectively, the characterization of the lignin and lignin residues by GPC and NMR [24,25], has to be carefully performed

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in order to understand the evolution of the organic functions and the macromolecule size during the transformation. In addition, the characterization of the complex bio-liquid requires specific technique as the comprehensive two-dimensional gaseous chromatography (GC × GC), in order to properly separate, identify and quantify the numerous components [26]. Several research groups have developed so far the use of this technique for lignin bio-liquids and deep improvement of valuable liquid fraction characterization was reached, allowing to investigate the reaction mechanism at a molecular level [16,17,20,27].

The hydroconversion of a wheat straw soda lignin with a $NiMoS/Al_2O_3$ catalyst in H-donor solvent was previously successfully undertaken in a batch reactor, and a product recovery protocol with 98 wt% mass balance was reported [28]. A set of analytical tools including NMR (^1H, ^{13}C, ^{31}P, HSQC), GPC and GC × GC were used to characterize the starting lignin, the lignin residues and the liquids. After 5 h of residence time, 65 wt% of liquid and 10 wt% of gas were obtained from the soda lignin. Catalytic role was demonstrated by comparing two experiments with and without catalyst. Even if the non-catalytic experiment led to a significant conversion rate (52 wt%) and liquid fraction yield (32 wt%), the composition varied drastically compared to the catalytic experiment. In the non-catalytic experiment, all the products were oxygenated compounds while hydrodeoxygenation was observed in the presence of the catalyst.

In the present work, keeping the same quite low catalyst-to-lignin ratio (10 wt%), we especially pay attention to the impact of residence time (from t0 up to 28 h) on the lignin reactivity as it has been observed that, after 5 h of residence time, the NiMoS catalyst was still active and the lignin residue and the oligomers in the liquid can be further converted. Lignin residues were thus fully characterized for each residence time by NMR including 2D-technique HSQC and liquids composition was carefully investigated by GC × GC/MS and GC × GC/FID for qualitative and quantitative purposes respectively.

2. Materials and methods

2.1. Materials

Protobind 1000 lignin was produced by soda pulping of wheat straw and was supplied by Green Value (Switzerland). The reagents used were 1,2,3,4-tetrahydronaphthalene (tetralin) (Sigma–Aldrich, ReagentPlus®, 99%), acetone (Sigma–Aldrich, CHROMASOLV®, for HPLC, ≥99.9%), dimethyl disulfide (Sigma–Aldrich, ≥99.0%), pyridine (Carlo Erba, purum, ≥99.9%), acetic anhydride (Prolabo, analytical grade), tetrahydrofuran (Sigma-Aldrich, analytical grade, ≥99.9%), *n*-heptane (Carlo-Erba, 99.2% pure) and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Sigma–Aldrich, 95%), $CDCl_3$ (Sigma–Aldrich, 99.8% atom D), DMSO-d6 (Sigma–Aldrich, 99.9% atom D). The compounds used as reference compounds for product identification by gas chromatography (hydrogen, carbon monoxide, carbon dioxide, methane, ethane, propane, *n*-butane, isobutene, pentane, isopentane, hexane, 2-methylpentane, ethylene, propylene, 1-butene, 1,3-butadiene, 1-pentene, 1-hexene), were of analytical grade. The chemicals were used as received.

The catalyst used in this study was a NiMo catalyst supported over γ-alumina (shaped as extrudates), supplied by IFP Energies nouvelles (Solaize, France). This catalyst obtained by incipient wetness impregnation is composed by NiO (3 wt%), MoO_3 (16 wt%) and P_2O_5 (6 wt%) and the BET surface area was 181 m^2/g. Activation of the catalyst was performed ex situ at 400 °C (ramp of 5 °C/min) for 150 min under a flow (4 L/h) of H_2/H_2S (15 vol% H_2S).

2.2. Characterizations

For C, H, O, N and S content measurements, a Thermo Scientific Flash 2000 apparatus was used. Oxygen was measured after pyrolysis by quantification of CO by a thermal conductivity detector. Carbon, hydrogen, nitrogen and sulfur were measured after combustion and separation of CO_2, H_2O, SO_2 and NO_x, and quantification of these gases by a thermal conductivity detector. Other elemental analyses (metals) were performed by ICP-AES after solubilization of samples in acidic solutions using an Activa apparatus from Horiba Jobin Yvon.

Gel permeation chromatography (GPC) analyses were based on previously developed methods for lignin molecular weight determination [29,30]. Analyses were performed by using an Agilent apparatus (1200 series) equipped with two PL gel columns (50 and 500 Å) and a differential refractive index (DRI) detector. Analyses were carried out at 35 °C using THF as eluent at a flow rate of 1 mL/min. Acetylated samples were dissolved at around 5 wt% in THF before injection. The GPC system was calibrated with polystyrene standards with molecular weights from 162 to 55,100 g mol^{-1}. Depicted chromatograms were normalized to the sample weight. The lignin residues obtained after each hydroconversion run were completely soluble in THF and did not need to be acetylated.

^{31}P NMR technique was used for the characterization and the quantification of OH groups on the basis of previously developed methods involving a prior derivative phosphitylation step [31]. Samples were accurately weighted (c.a. 30 mg) and dissolved in a solution containing 200 mg of pyridine, 100 mg of an internal standard solution in pyridine (cyclohexanol, 15.7 mg/g), 100 mg of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, and 200 mg of $CDCl_3$. ^{31}P NMR data were obtained with a Bruker Avance (250 MHz (^1H) 75 MHz (^{13}C)) probe QNP (Quad Nucleus Probe) 5 mm. The phosphorous atoms bounded to former alcohol or phenols have different chemical shifts that enable to quantify each OH group.

The ^1H, ^{13}C NMR techniques enable basic structural characterizations. Around 50 mg of sample was dissolved in 700 mg of DMSO-d_6 using a Bruker Avance (250 MHz (^1H) 75 MHz (^{13}C)) probe QNP (Quad Nucleus Probe) 5 mm and Topspin 2.1 Bruker Software. ^1H spectra were acquired with single pulse acquisitions, ^{13}C spectra with inverse gated decoupling. Hetero-nuclear single quantum coherence (HSQC) experiments allow identification of lignin structural units and the inter-unit patterns. The 2D HSQC were obtained on a Bruker Avance (600 MHz (^1H) 150.9 MHz (^{13}C)) probe BBI (Broadband inverse) 5 mm and Topspin 2.1 Bruker Software. The HSQC pulse sequence is based on proton and carbon bonding via J^1_{C-H} coupling constants. All the acquisitions were done by heating the samples at 50 °C. Due to broad and overlapping signals, only relative quantifications were obtained by ^1H and ^{13}C NMR while ^{31}P NMR allowed absolute quantification thanks to the use of an internal standard.

The μGC-TCD-MS technique was used to characterize gases formed during lignin hydroconversion. The gas phase was recovered in tedlar bags after cooling down the reactor at room temperature and compounds were separated with a μGC Agilent 5975C apparatus equipped with three columns. A 5 Å molecular sieve column (10 m, 12 μm) was used to analyze H_2, CH_4 and CO; the carrier gas was argon; the backflush injector temperature was maintained at 80 °C, the inlet is heated at 100 °C and the column temperature was kept at 90 °C. A Poraplot U column (8m, 30 μm) was used to separate CO_2, ethane, ethylene and H_2S; the carrier gas was hydrogen; the backflush injector temperature was maintained at 90 °C and column temperature was kept constant at 80 °C. An alumina column (10 m, 3 μm) was used to analyze C3 to C6 hydrocarbons; the gas carrier was hydrogen; injection temperature was

maintained at 100 °C, while column temperature was kept constant at 90 °C. Two detectors were used: a mass spectrometer for identification (connected to Poraplot and Alumina columns) and a TCD detector for quantification.

Two-dimensional gas (GC × GC) MS chromatograms were recorded using an Agilent 6890 apparatus with a liquid nitrogen cryogenic jet modulation from Zoex Corporation coupled with a 5975B qMS (Scan parameters: from 45 to 300 μ at 22 scan/s) detector, this system has been previously fully described [32]. The combination of columns was adapted from the reverse system proposed for the analysis of phenols and oxygenates in coal derived liquids [33].

The first column was a moderately polar VF1701 column (30 m × 0.25 mm × 0.25 μm) and the second column was an apolar DB1 column (2 m × 0.1 mm × 0.1 μm). The temperature program of the first oven started at 50 °C for 5 min and then was heated up at 1.75 °C/min until 300 °C. The second oven started at 50 °C for 0 min and then heated up at 1.8 °C/min until 307 °C and at 1.8 °C/min until 320 °C. The modulation time was 12 s and the modulator hot jet temperature was set to 280 °C. The NIST-MS 2011 database was used for peak identification. Samples were injected without any prior dilution.

GC × GC/FID analyses were carried out using the same columns set on a Pegasus III instrument (LECO, Saint Joseph, MI, USA) equipped with a FID. Modulation was performed with a dual stage-four jet modulator fed with liquid nitrogen. The modulation period was 7 s and the temperature hot jet was 60 °C superior to the oven temperature. Separation was accomplished by using a temperature ramp (2 °C/min) from 50 °C to 300 °C and a constant carrier gas (He) flow of 1.8 mL/min. 0.5 μL of neat sample were injected in a split/splitless injector at 320 °C with a 1:100 split ratio. Detector temperature was set to 320 °C with hydrogen and air flow rates of 40 an 450 mL/min respectively and helium as a make-up gas (50 mL/min). Quantification was performed using homemade 2DChrom software (IFPEN, Solaize, France) and using ECN to model FID response factors for identified compounds.

For High temperature GC × GC, an Agilent 7890A apparatus equipped with a switch valve modulator was used as described in [34]. Chromatograms were recorded with the following set up: a first apolar column DB1-HT (15 m × 0.1 μm × 0.1 mm) and a second polar column BPX50 (5 m × 0.25 μm × 0.25 mm) and a flame ionization detector (FID) was used. The program of temperature was 40 °C (8 min); 2 °C/min 360 °C (5 min); for the oven 1, and 50 °C (8 min); 2.25 °C/min 360 °C (27 min); for the oven 2. At 50 °C/mn. The injection volume was 1 μL. The modulations (8 sec) were carried out by capillary flow technology from Agilent.

2.3. Hydroliquefaction experiments

As previously described [28], the hydroliquefaction experiments were undertaken in a 300-mL stainless steel high pressure Parr batch reactor equipped with a 2 L H_2 ballast and pressurized at 8 MPa. The temperature was set to 350 °C and monitored using a thermocouple and mechanical stirring was performed using a hollow-shaft six-bladed turbine at 800 rpm. 30 g of lignin (dried at 60 °C under vacuum for 1 h) was introduced in 70 g of tetralin with 3 g of freshly sulfided $NiMoS/Al_2O_3$ catalyst and 16 μl of DMDS. DMDS was added to maintain the sulfidation state of the catalyst since the sulfur content of the feedstock was quite low, resulting in a low H_2S partial pressure in the reactor. The DMDS contribution in the production of methane and H_2S has been removed from the produced gases distribution. Residence times of 1 h, 14 h and 28 h were used for the present study in addition of the time zero t0 (time to reach the reaction temperature) and t = 5 h already reported. After each experiment, the cooling down procedure previously fully described was systematically applied and the mass balance reached up to 98 wt% (+/−3.5 wt%). Before opening the reactor, the gases were recovered in 5 L tedlar bags and analyzed with μGC-TCD-MS apparatus.

The products recovery protocol already described in the previous work was applied. For all the runs, the ash-free conversion was defined as the ash free lignin conversion to THF soluble products and gases, calculated according the following equation:

$$\text{Conversion}=(1-\frac{w(\text{THF}-\text{solubles})+w(\text{THF}-\text{insolubles})}{w(\text{initialLignin}-\text{ash})})\times 100$$

where w(THF-insolubles) is the weight of the solids obtained in the Soxhlet cartridge without the catalyst, w(THF-solubles) is the weight of solids recovered after THF evaporation and heptane precipitate from the liquid products, w(initial lignin) is the initial weight of lignin used, and w(ashes) is the weight of ashes in the initial lignin.

H_2 consumption during the reaction was determined from the initial quantity of hydrogen introduced in the batch, the quantity of H_2 introduced during the experiment from the ballast (continuously monitored) and the final concentration of H_2 in the batch at the end of the experiment.

3. Results and discussion

Lignin hydroconversion experiments at various residence times (t_0, 1 h, 5 h, 14 h and 28 h) are described hereafter. Since the gap of catalytic transformation between t0 and 5 h (75 wt% of conversion of the ash-free lignin including 10 wt% of gases and 65 wt% of liquids) was already significant [28], an additional 1 h reaction time experiment was performed to evaluate the intermediate conversion, the liquid composition and the impact of a short residence time on the lignin residue structure. Longer residence times (i.e. 14 h and 28 h) were carried out in order to reach the highest conversion level, to assess the deactivation of the catalyst and to evaluate the impact on the products qualities. The evolution of the lignin conversion as a function of the residence time is given in Fig. 1, with additional information on product fraction yields and hydrogen consumption. It is clearly seen on this Figure, that both lignin conversion and liquid fraction yield have a similar trend. The lignin conversion increased from 28 wt% at t0 up 87 wt% after 28 h, with 71 wt% of produced liquid while the lignin residue (THF-solubles) yield decreased from 65% at t0 down to 11.4 wt% after 28 h. We can also observe that the gaseous fraction yield is almost constant above 5 h (around 10 wt%). The solids (THF-insolubles) yield also reached a plateau after 1 h which corresponds to a slightly higher value than the ashes content in the initial lignin (5–6 wt% of the total initial lignin vs 4 wt% for ashes). The excess of solids (around 1 wt% reported on Fig. 1), by comparison with initial ashes content can be considered as char. As expected, the hydrogen consumption increases with the conversion level. However, between 14 h and 28 h of residence time, the conversion of lignin and the H_2 consumption stayed at the same level, suggesting that after 14 h, hydrogenation/hydrogenolysis reactions do not occur anymore. However, the conversion of tetralin to naphthalene, which can provide H_2 directly in the liquid phase (3 moles of H_2 per moles of naphthalene), was found to be close to 15% in the liquid fraction. This conversion ratio (Fig. S11) correspond approximately to 0.2 moles of H_2 potentially available in the liquid. Indeed, the H_2 coming from the dehydrogenation of the solvent could be directly involved in hydrogenation/hydrogenolysis reactions just after its formation in the liquid phase. It must be said that the chosen way to determine the lignin conversion does not take into account the changes occurring in the lignin residue as this lignin residue is considered as initial lignin for the calculations. The stability of the conversion between 14 h and 28 h of residence time only means that the lignin residue is not cleaved sufficiently to be further sol-

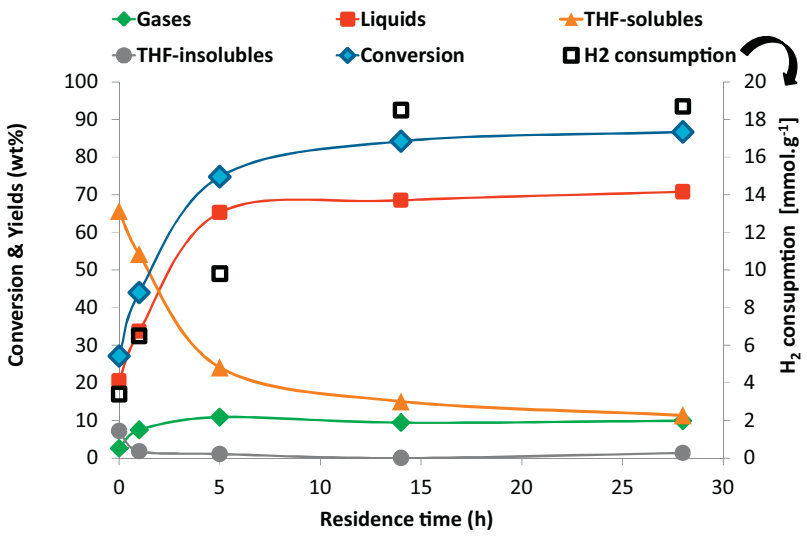

Fig. 1. Evolution of lignin conversion (ash-free lignin), yields of the different fractions and H_2 consumption as a function of residence time over $NiMoS/Al_2O_3$ at 350 °C.

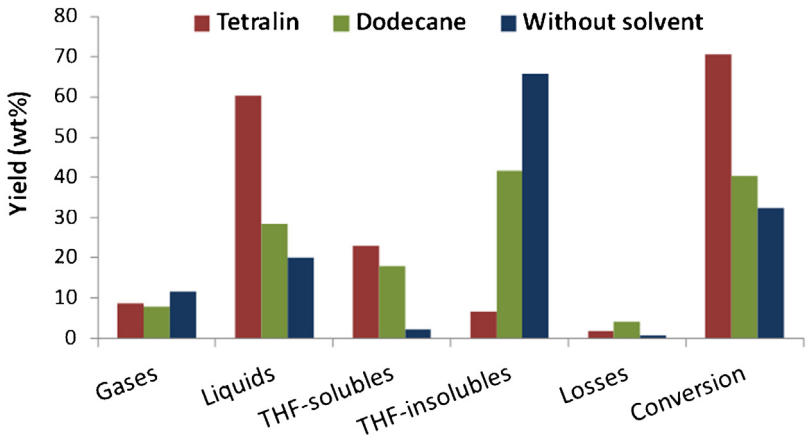

Fig. 2. Lignin conversion and yields in gas, solid and liquid fractions with tetralin, dodecane solvent or without any solvent.

Table 1
Elemental composition of the solid fraction (THF-insolubles) as a function of the residence time.

Element (wt%)	0 h	1 h	5 h	14 h	28 h
C	58.7	53.5	53.4	41.4	38.8
H	4.2	3.3	3.3	2.3	2.6
O	22.9	16.6	13.7	18.4	13.1
N	1.7	2.3	2.1	1.9	1.8
S	1.5	3.0	3.0	5.0	4.7
Inorganics[a]	11	21.3	24.5	31	39

[a] Values obtained by subtraction of the organic fraction (can be considered as ashes content).

ubilized in the liquid phase. The O decrease in the lignin residue between 14 h and 28 h of residence time (Table 2), the strong increase of benzene and naphthenes derivatives in the liquid fraction after 14 h (Fig. S5) and the evolution of the OH functional groups confirmed that H_2 was still available and involved after 14 h of residence time in hydrogenation/hydrodeoxygenation reactions.

The characterization of the lignin residue is thus highly necessary to evaluate the transformation which takes place during this time. Furthermore, the changes observed for the molecules distribution in the liquid phase between 14 h and 28 h of reaction attest that H_2-involved reactions still occur. The role of tetralin solvent was clearly shown by two experiments: the first one with dodecane instead of tetralin and the second one without any solvent (Fig. 2). After 5 h of reaction, in dodecane, the total conversion was only 40 wt% compared to 71 wt% with tetralin solvent and in addition, higher yield of solid residues (45 wt%) and lower yield of liquids (35 wt%) were obtained. The experiment without any solvent and involving the same amount of lignin than the experiments with tetralin or dodecane, showed a lower conversion and the presence of high amount of THF-insolubles. However the few differences observed between the use of dodecane solvent and the experiment without any solvent suggests that a non-polar solvent as dodecane was not appropriate for this kind of transformation. Comparatively, the use of tetralin favored oil formation and lower amount of solid residues.

3.1. Characterization of gas phase

The gas phase, analyzed by μGC-TCD-MS, was mainly composed of CH_4, CO_2, light alkanes with C2–C6 carbons, and traces of CO (Fig. 3). The presence of CO_2 and CO can be easily explained by the decarbonylation/decarboxylation and water gas shift reactions, the presence of CH_4 by demethylation and methanation reactions, this latter being thermodynamically favored in these conditions [35]. The light alkanes came from the C–C cleavage (hydrogenolysis) of the short alkyl chains of the lignin. After a maximum yield at 1 h, production of CO decreased to a very low level and was not

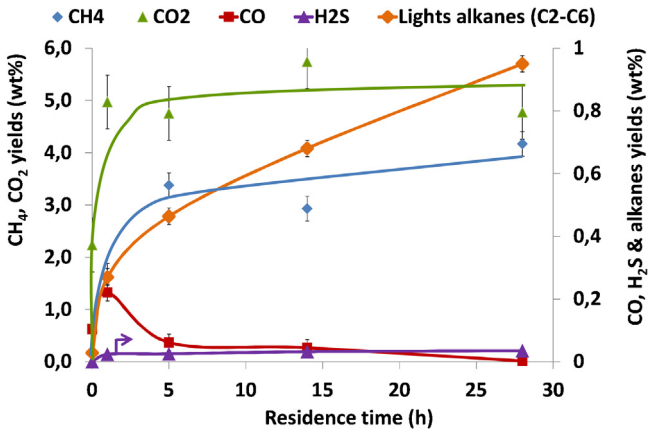

Fig. 3. Gas-phase composition according to the residence time.

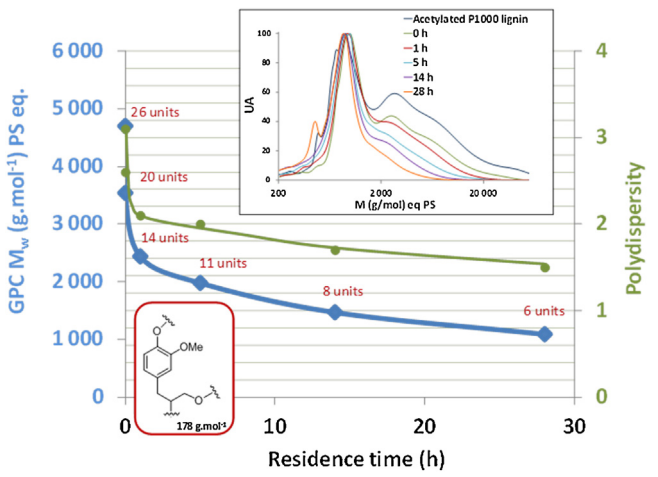

Fig. 4. Evolution of lignin Mw and polydispersity (by GPC) as a function of the residence time considering an arbitrary unit in polystyrene (PS) equivalent.

detected anymore after 14 h. Between 5 h and 28 h, carbon dioxide and methane yields are stable while light alkanes yield slightly increase. Here again, the increase of the light alkanes between 14 h and 28 h of residence time indicate that hydrogen was still consumed despite the observed plateau for the total H_2 consumption. All these reactions were enhanced or displaced by the presence of the catalyst as previously observed.

3.2. Characterization of char and ash (THF-insolubles)

Due to the low amounts and the insolubility of these solids in classical solvents including THF, only CHONS elemental analyses were performed on the solid fraction (Table 1). The oxygen content decreased from 23 wt% to 13 wt% in 28 h while the C and H contents remained at around 40 wt% and 2.5–3 wt% respectively. Unsurprisingly, the inorganic content, evaluated by subtraction of the organic phase, increased in function of the residence time. After 28 h, the CHONS content represents only 61 wt% of the solids, which means that inorganic content in this fraction reaches 39 wt%. The inorganics present in this lignin (i.e. mainly Si and Na) were previously identified by MEB and elemental analysis. Indeed, after this residence time, the solid yield is quite low and close to the ashes content in the initial lignin (5 wt% including ashes) indicating that, under these operating conditions, the lignin conversion does not lead to solids formation via condensation/polymerization reactions.

3.3. Characterization of lignin residue (THF-solubles)

Lignin residue is a partially converted lignin fraction which became completely soluble in THF and then is defined as THF-soluble fraction. Lignin residue conversion after 5 h of residence time shows deep cleavage and chemical transformation, especially via deoxygenation reactions. After 28 h of residence time over the supported NiMoS catalyst, the lignin residue represented 11 wt% of the ash-free starting lignin. The structure modifications of the lignin residue were characterized at each stage of the reaction by using Gel Permeation Chromatography (GPC) which was calibrated with polystyrene (PS) standards. Arbitrarily, it was considered that lignin residue was made of hydroxypropyl-guaiacyl units with a molecular mass of 178 g mol^{-1}, as the generally admitted structure of initial lignin. The GPC analyses carried out on the residues produced at different reaction times indicated that the 26 units for the initial lignin were progressively transformed into a lignin residue containing 20 units in PS equivalent after reaching the reaction temperature (t_0) and to 6 units after 28 h of reaction time (Fig. 4). This evolution confirmed that lignin residue was converted by cleavage versus time, decreasing its average molecular weight, as well as its polydispersity (from 3.1 to 1.5). For the lignin residue after 28 h, we can also observe that the final main peak is centered around 890 g mol^{-1} (in PS equivalents) not so far from the first peak of the bimodal distribution already measured in the starting lignin. This domain of molar mass is also close to the one determined for a typical pyrolytic lignin [36]. In our experiments, the decrease of the model units arised together with the decrease of the oxygen content (Table 2). By the same time, the carbon content increased and then the O/C atomic ratio reached 0.06 after 28 h against 0.32 in the starting material while the H/C atomic ratio remained constant around 1. The lignin residue is thus progressively deoxygenated by several reaction pathways. Compared to the initial lignin, 50% deoxygenation level was reached after 1 h of reaction and 81% of oxygen removal was obtained after 28 h. Using HSQC NMR data, it has been already shown in our previous paper, that after 5 h of reaction, the O—C_{aliph} ether bonds were totally cleaved while aliphatic double bonds were hydrogenated, and aliphatic OH groups were removed by dehydroxylation. It has been also observed that methoxy groups were progressively removed from lignin residue while phenolic hydroxyl groups were partially converted but still present after 5 h of reaction time. The evolution of the different chemical functions at other residence times completes these observations. For instance, only guaiacyl and phenolic units increased after 1 h of residence time, these units being still present in the lignin residue after 5 h of conversion as shown by the evolution of ^{31}P NMR spectra after phosphytilation (Fig. 5). The syringyl and condensed OH units cannot be distinguished by this technique. However, the total disappearance of syringyl units was observed by HSQC. Thus, the remaining part of ^{31}P signals after 5 h of residence time should only correspond to condensed OH units. By increasing residence time, guaiacyl units of the lignin residue were progressively converted to catechol (benzenediol) by demethylation or to phenol unit by methoxy group removal (demethoxylation reaction). Then, as observed for guaiacol hydrodeoxygenation reaction (HDO) studies over sulfide catalysts [37], catechol units were successively dehydroxylated to phenol and phenol to benzene or cyclohexane units. However, the observed solubility of the lignin residues decreased strongly according to the residence time, and the liquid NMR spectra of the lignin residues after 14 h and 28 h were not relevant to assess the structures. Because of the complexity of the mixture, we were not able to evidence if demethylation or demethoxylation was favored under these conditions. However, the presence of catechol units detected on the lignin residue indicates that demethylation reaction from guaiacyl group occurs. The demethoxylation was evi-

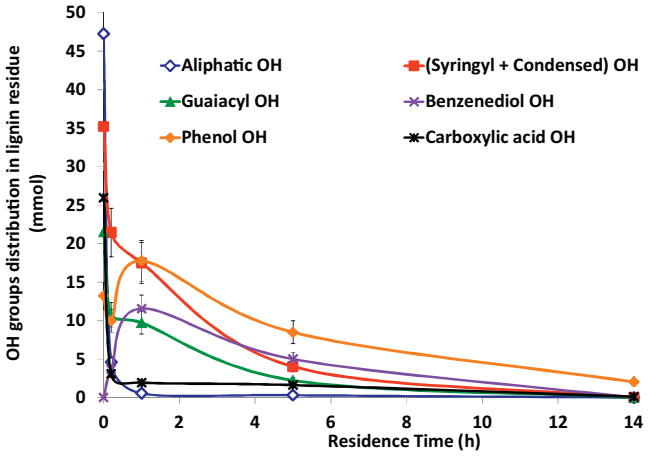

Fig. 5. Evolution of OH functional groups of lignin residues by ^{31}P NMR after phosphytilation as a function of residence time.

denced by the increasing amount of guaiacyl units as syringyl units were disappearing. In HSQC NMR experiments, only the aliphatic region still shows some signals (Supplementary material, Fig. S1) which correspond to the presence of aliphatic chains due to the deoxygenation process; no signal in the aromatic and oxygenated aliphatic regions was observed. This lack of signal is maybe due to the low sensibility of the two-dimensional analytical technique as, the aromatic carbons, which are undoubtedly present, probably in condensed form, were still observed by solid NMR (Fig. S2) and aromatic protons in 1H spectrum (Fig. S3).

3.4. Characterization of the liquid product

The liquid products yield, corrected from tetralin contribution, reached 71 wt% after 28 h of residence time over supported NiMo catalyst. The liquid fraction was analyzed by GC × GC/MS. Thanks to a recently developed system which involves a first moderately polar column (VF-1701-MS) and a second short column (DB1), a much better separation of the numerous compounds was obtained, compared to the previous work using conventional columns system [28]. In particular, the separation of the phenolic products from the tetralin solvent was highly improved (Fig. 6). The following main families of products were clearly distinguished: alkanes, naphthenes, aromatics, phenols, methoxyphenols, dimethoxyphenols, benzenediols, biphenolic compounds in addition to tetralin and naphthalene derivatives formed during the conversion. Additionally, minor families or isolated products like: anisoles, cyclohexanone, other ketones, heptanol, and anilines were also evidenced (Fig. 6). Alkanes higher than nonane were detected despite not expected in the liquid phase. The presence of these alkanes was explained by the hydrogenation of C16–C18 fatty acids and esters which have been detected in the liquid phase after short reaction time. Those fatty acids or esters are probably coming from some cutin or suberin moieties, some lipophilic polymers present in the initial wheat straw and which are composed by C16 to C18 esters (Fig. S4) [38]. Inside the main families, a more detailed molecular identification has been performed thanks to the MS detector. For instance in each family (phenols, aromatics, cyclohexane...), molecules with a C1, C2, C3, C4 or C5 alkyl substituent were distinguished. Additionally, the nature and the number of substituent can sometimes be attributed in accordance with the MS database. Some of the methyl, ethyl and propyl-

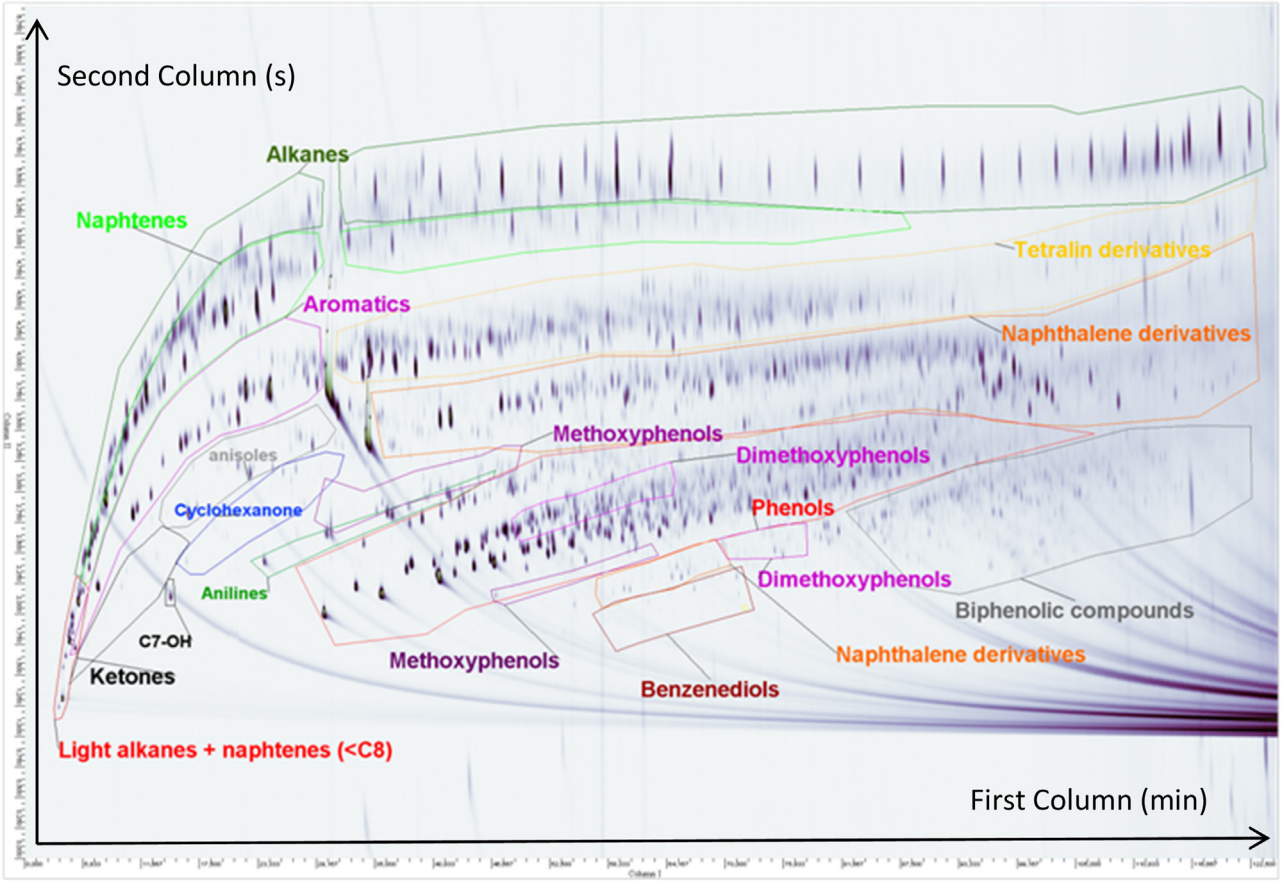

Fig. 6. GCxGC–MS chromatogram of the liquid fraction after 28 h of reaction.

Table 2
CHONS elemental analyses and H/C, O/C and N/C atomic ratios for the lignin and lignin residues (standard deviation values in brackets).

			Residence time				
	Element (yield wt%)	Lignin P1000	0 h (59 wt%)	1 h (52 wt%)	5 h (23 wt%)	14 h (15 wt%)	28 h (11 wt%)
wt%	C	62.5 (±0.5)	68.9 (±0.4)	75.4 (±0.5)	80.2(±0.5)	81.1(±0.5)	83.5(±0.5)
	H	5.9 (±0.1)	5.5 (±0.1)	6.6 (±0.1)	6.0 (±0.1)	6.4 (±0.1)	7.5 (±0.1)
	O	27.0 (±1.5)	24.0 (±1.4)	15.9 (±0.9)	11.1 (±0.6)	8.7 (±0.5)	6.9 (±0.4)
	N	1.2 (±0.1)	1.4 (±0.1)	2.0 (±0.1)	2.6 (±0.1)	2.5 (±0.1)	2.0 (±0.1)
	S	0.1 (±0.1)	0.0 (±0.1)	0.0 (±0.1)	0.1 (±0.1)	0.0 (±0.1)	0.6 (±0.1)
	Total	96.7 (2.3)	99.8 (±2.1)	99.8 (±1.7)	100.1 (±1.4)	98.7 (±1.3)	100.5 (±1.2)
Atomic ratios	H/C	1.12	0.96	1.05	0.90	0.95	1.08
	O/C	0.32	0.26	0.16	0.10	0.08	0.06
	N/C	0.016	0.022	0.028	0.028	0.020	0.017

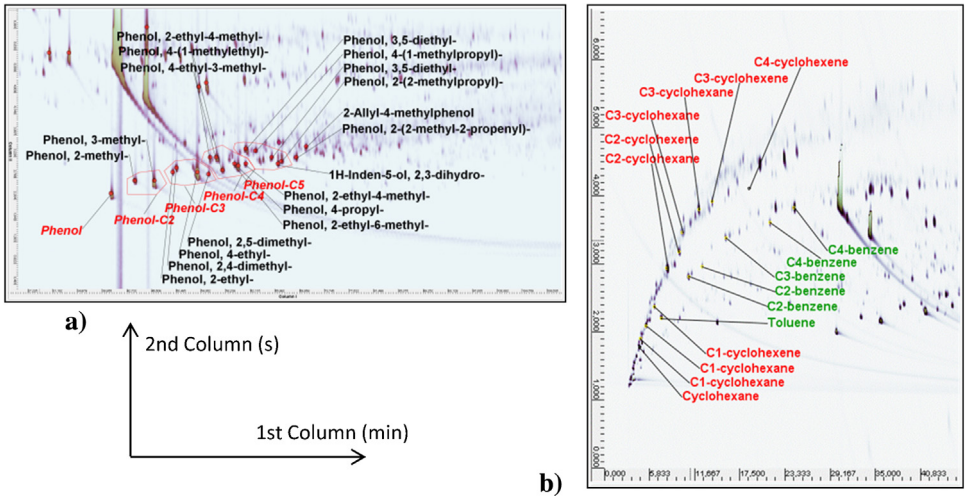

Fig. 7. Detailed identification of (a) phenolic; (b) naphthenic and aromatic compounds of the liquid phase in the enhanced view of GCxGC–MS chromatogram.

substituted phenol compounds formed during the experiment and identified by GC × GC/MS are detailed in Fig. 7a. The same type of identification was performed for the aromatic and naphthenic compounds (Fig. 7b). We thus observed the formation of C1- to C4-substituted cyclohexane, cyclohexene, and benzene. In a second step, quantification was achieved by performing additional GC × GC/FID analyses on a similar set-up and by using equivalent carbon number (ECN) model to predict FID response factors of hydrocarbons and oxygenated compounds [39]. The evolution of the yields of dimethoxyphenols, methoxyphenols, benzenediols, phenols, aromatics, naphthenes, and alkanes families as a function of the reaction time is reported on Fig. 8. As expected, while (di) methoxyphenols and benzenediols rapidly disappeared, the phenols yields increased continuously and reached 11 wt% of the starting lignin after 28 h. Paraffins, naphthenes and aromatics yields also both increased in parallel to reach a total of 13.3 wt% of the initial lignin. The quantitative data obtained for the different families of products are given in supplementary material (Fig. S5). In each family, except for dimethoxyphenolic compounds, the C2 (mainly ethyl) substituted compound was observed to be the main component. The occurrence of these C2 products and the few amount of lights alkanes in the gas-phase, suggests the presence of ferulic acids or benzofuran units in the starting lignin, these two precursors being converted into ethyl phenol by hydrodeoxygenation (Figs. S6 and S7). According to this quantification, the main compound in the liquid phase was 4-ethylphenol, indicating the predominance of the ferulic units in the initial Protobind 1000 lignin. Besides, in the starting material, the presence of these precursors (ferulic, benzofuran) was observed using HSQC NMR, but not quantified.

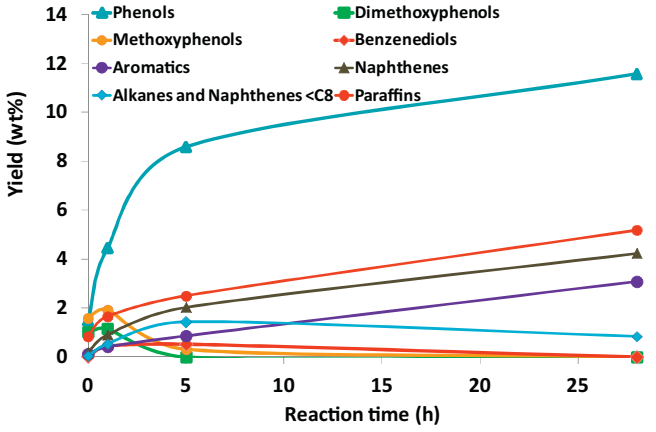

Fig. 8. Evolution dimethoxyphenols, methoxyphenols, benzenediols, phenols, lights hydrocarbons, paraffins, naphthenes and aromatics according to the reaction time.

3.5. Additional comments

The reaction scheme already published for model molecule studies showed that demethoxylation, dehydroxylation and double bonds hydrogenation leading successively to phenolic, aromatics and naphthenic products were the main reactions observed in the catalytic HDO of guaiacol with metal sulfide catalysts [37]. In this work, the catalytic hydroconversion of the wheat straw soda lignin in tetralin solvent lead to monomers and oligomers, mainly in the liquid phase. The identification of monomers products confirmed that the lignin liquefaction over a supported NiMoS catalyst implies

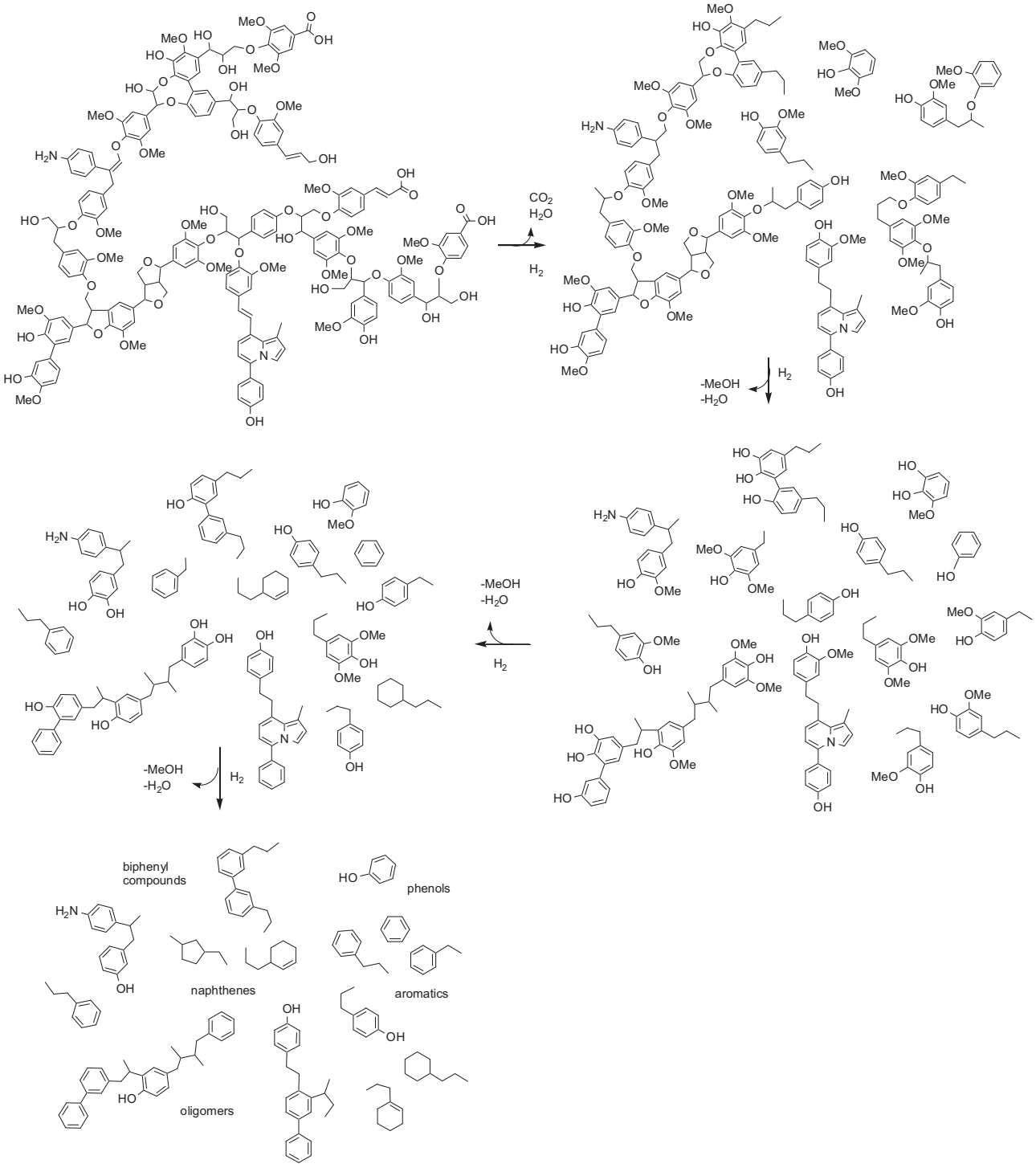

Fig. 9. Progressive transformation scheme of lignin to oligomers and monomers under catalytic hydroconversion with $NiMoS/Al_2O_3$.

a similar reaction pathway when compared to the one observed for guaiacol HDO and thus confirm the interest for choosing guaiacol as a representative model compound to mimic lignin reaction scheme. However, chemical complexity could have a strong impact on the catalytic activity and selectivity of the catalysts, when compared to the model studies. Concerning the solvent effect and regarding the low amount of solids (char) obtained with tetralin solvent by comparison with the use of dodecane, these experiments also clearly indicated that the use of a H-donor solvent is very helpful to depolymerize the wheat straw lignin since condensation reactions are limited.

The best achievement in this study is the extensive use of GC × GC to identify most of the components in the complex liquid phase. However, the total quantified monomeric and dimeric products did not exceed 40 wt% of the liquid phase. The complexity of the mixture, the presence of tetralin and its derivatives which can mask some chemicals in the 2D chromatogram, as well as the evaporation of the lighter products during the product recovery protocol can partially explain this result. In addition, the liquid phase must contain unidentified soluble oligomers which are not eluted during GC × GC analysis as reported recently [20]. A high temperature GC × GC/FID analysis performed on the liquid phase

Table 3
C, S elemental analysis, BET surface area, pore diameter and pore volume for (28 h) used and fresh catalyst.

	Fresh catalyst	Used catalyst (28 h)
C (wt%)	0	11
S (wt%)	9	6
BET surface area ($m^2\ g^{-1}$)	219	199
d_p (nm)	9.1	5.3
V_p ($cm^3\ g^{-1}$)	0.5	0.26

obtained after 5 h reaction showed that some of the components of the liquid phase were effectively not detected by the usual GC × GC system. These compounds were located in the area of heavy alkanes and biphenolics (Fig. S8). The distribution of the detected alkanes (C9 to C31) as a function of the residence time is reported in Fig. S9. The heavier alkanes (C30–C35) were probably formed by the ketonization reaction between two C16–C18 fatty acids in the liquid phase and further hydrogenation. Additionally, the GPC analysis of the liquid phase after 14 h of reaction, indicated that this fraction contains some heavy products centered at 840 g mol^{-1} in PS equivalents (Fig. S10). The lignin residue also contains this kind of fragments (or slightly heavier) which can probably become soluble in liquid depending of the remaining organic functions and the molecular size. Except for the size, we assume that the molecular structure of the lignin residue and the heavy products of the liquid phase are very similar.

In addition to a better knowledge on the hydroconversion process of a real lignin feed in tetralin solvent, these experiments allowed us to assess-back the structure of the studied lignin according to the molecular nature of the products in the liquid phase. Hence, several conclusions can be given on the lignin structure:

- The β-O-4 linkages were not observed by HSQC after 5 h conversion on the lignin residue, but the lignin residue is still a macromolecule which consists in 16 units in PS eq. This suggests that, in the initial lignin, the units are not bounded exclusively by β-O-4 ether linkages, known to be the most abundant bonds in this type of macromolecule. Stronger C—O and/or C—C bonds, which are more difficult to identify, exist in the initial structure certainly due to the pretreatment used to isolate the Protobind lignin. If all the units were linked by β-O-4, ether bond which is one of the easiest to cleave, all of those would be readily cleaved and we would observed a complete depolymerization after a few hours of residence time.
- The ferulic units must be present in high amount in the initial lignin as the 4-ethylphenol is one of the most abundant phenol derivatives in the liquid mixture.
- Fatty ester or acids are present in quite large amount as C16–C18 alkanes were observed up to 5.2 wt% of the initial lignin in the liquid phase. The formation of those alkanes being in relation with the presence of cutin- or suberin-like moieties in the lignin fraction. These additional entities must be taken into account while studying lignin conversion.

The catalyst used for 28 h was characterized and compared to the fresh sulfide catalyst (Table 3). Unsurprisingly, the carbon content increased while the sulfur content decreased for the used catalyst. The BET surface area was slightly lower, as well as the average pore volume and diameter. However, the evolution of BET surface area, pore volume and diameter in function of the residence time (Figs. S12 and S13) showed that the main changes occurred during the first hour of the hydroconversion and then the catalyst did not change much. It is quite interesting to note that compared to many works in lignin liquefaction in solvent, the quite low catalyst-to-lignin ratio used here (10 wt%) allowed to convert the lignin without being fastly deactivated.

Finally, in our operating conditions, without any information on the lignin solubility in tetralin, it can be assumed that the initial degradation of the lignin is mostly thermal and then become catalytically driven as soon as oligomers can interfere with the catalyst. During the initial thermal step carboxylic acidic functions of the initial feed started decarboxylation, the weakest β-O-4, α-O-4 ethers linkages were cleaved and dehydration of the aliphatic OH groups took place (Fig. 9). Then, in a second time, the catalytic stage began with the hydrogenation of double bonds on aliphatic chains and the demethoxylation, demethylation and dehydroxylation of phenols to form progressively phenolic, aromatic and naphthene monomers and oligomers in the liquid phase.

4. Conclusion

In this study, catalytic lignin hydroconversion performed in a H-donor solvent lead to a high conversion level mainly in liquid. A deep deoxygenation was observed both for lignin residues and liquids, the same type of reactions being observed in both fractions. After the longest residence time, the liquids contain mainly phenols, aromatics and naphthenes monomers which perfectly match with the products observed from model guaiacol HDO studies. Those identified monomers, in addition to the long-chain alkanes coming from the hydrogenation of fatty esters, represent 25 wt% of the initial lignin after 28 h. However, a significant part of the high molecular weight liquid fraction was not identified certainly due to the presence of soluble oligomers which are not eluted during the GC × GC analysis. Our effort will be further focused on the characterization and the deeper conversion of the oligomers that are still present in the liquid phase.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2015.11.005.

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